

Sulfur partition by process stages of metallurgical production of JSC EVRAZ NTMK

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Abstract. The current level of development of the industry requires the manufacture of steel with high purity in relation to detrimental impurities. Sulfur is one of such impurities that significantly reduces the service properties, the content of which is strictly regulated in the finished product. Deep desulfurization may be achieved through development of cross-cutting technology of metal production as a single process including agglomeration and blast-furnace process and steelmaking. Sulfur partition by metallurgical process stages via conversion from raw materials of the blast-furnace process to steel continuously cast blank is studied in this work. It is shown that removal of sulfur from the half-finished product at the desulfurization plant will not provide the required sulfur content (less than 0.005 %) in the steel ingot. It is determined that the activity plan comprising treatment of the half-finished product at the desulfurization plant, smelting in the converter, treatment of steel at the ladle furnace unit and then in the vacuum vessel is required to obtain the final content of sulfur of less than 0.005%.

1. Introduction

Modern consumer of metallurgical products imposes increasingly demanding requirements to the produced steel quality. Sulfur is subjected to the strictest limitations on content in metal [1]. Significant number of theoretical and practical works is dedicated to deep desulfurization of metal in order to obtain low sulfur content in the finished products. This direction has special actuality for production of high-strength steels (pressure vessels, oil and gas pipes of large diameter [2–4]), sheet steels for deep drawing [5, 6], reinforcement steels [7, 8], as well as mass-produced steels [9, 10]. Steels with the regulated low sulfur content are required for aviation, power and transport engineering, construction and other industrial fields [11–13].

Normally increase of requirements to steel properties outstrips development of processing methods aimed at improvement of metal purity. As a result, it is necessary to search for combinations of efficient methods of refining for all types of process stages of metallurgical production. Currently, not



a single type of metallurgical raw materials is used without preliminary preparation, which allows to carry out measures for sulfur removal at the stage of preparing the charge materials for blast-furnace smelting [14, 15]. Behavior of sulfur during agglomeration of iron-ore materials is well-studied, therefore, in case of correct process organization, a high sulfur removal rate will be achieved ensuring structural and other characteristics of agglomerated materials. Major part of work for removal of sulfur from metal is carried out in the blast-furnace process and during cast iron treatment afterwards. Continuous mode of desulfurization implemented in the blast furnace is the most efficient among all periodic processes offered alternatively. Cast iron quality becomes particularly important for the stage of converter operation where the possibilities of sulfur removal are limited [16–19].

Steel treatment at ladle furnace unit is an integral part of production of high-quality metal [16]; the technology provides induction of new high-basic free-running slag. Final concentration of sulfur in steel reduces together with increase of slag layer and its main basicity. Duration of argon blowing of the melt, increase of blowing rate and steel temperature result in reduction of sulfur concentration. Desulfurization conditions will deteriorate in case of increase of initial sulfur concentration and slag oxidation [17].

Special place of sulfur among other impurities included in steels is related to its impact on mechanical properties. Increase of sulfur content induces red shortness, decreases impact hardness, corrosion resistance, electric properties, and deterioration of plastic properties results in mass faulty production during stamping of deep-drawing hollow parts of sheet steel [1, 11, 18].

2. Theoretical data

Sulfur has unlimited solubility in the liquid iron (up to 38 % if its content in FeS is 36.5 %) and limited solubility in the solid iron: in γ -Fe at 1365 °C ~0.055%, and in α -Fe at 900 °C $\leq 0.015\%$ and at room temperature ~0.0001 % [1]. At transition of metal from liquid state to solid state, solubility of sulfur in it sharply decreases and continues to decrease at cooling of solid metal from crystallization temperature to room temperature. That is, hardening and cooling of metal with high sulfur content will lead to eutectic and release of FeS iron sulfide from the solid solution.

Fe-FeS eutectic has a low melting point (985 °C) compared to the temperature of the solidus of steel. In the presence of oxygen due to the formation of oxysulphides, eutectic crystallization occurs at even lower temperature. Presence of liquid state along grain boundaries in combination with contraction stresses of ingot and deformations of forging, rolling, etc. will lead to formation of cracks. Such phenomenon has been termed the ‘red shortness’. Sulfur may also have a negative influence on impact hardness of steel at low temperatures (less than –30 °C), embrittling metal. High sulfur content leads to sharp anisotropy of properties in the finished rolled products (Figure 1) [1]. Anisotropy of mechanical characteristics which depend on the mutual orientation of sulphide inclusions (orientation of sample relating to direction of rolling) is mostly demonstrated at plastic properties of metal, for example, relative elongation, relative reduction and especially impact hardness.

However, the Figure 1 shows that if sulfur content is less than 0.005 %, impact hardness of steel in transverse samples is significantly lower than in transverse ones, i.e. metal according to its properties becomes homogeneous at full volume.

Consequently, sulfur content of the metal, which does not influence the homogeneity of its properties is taken as not more than 0.005 %. However, in order to guarantee the absence of influence, its content must be even less and must not exceed 0.0001 % – the limit of dissolution of this element in iron at standard conditions [1].

Finished steel in some quantity contains all impurities that are part not only of metallic melting stock, but also of the slag and gas phases and lining, so the sulfur content in the final product depends on both the technology of production and the raw materials used. Conversion in metallurgy usually means the processing of material in which the chemical or phase composition of the product significantly changes its physical and mechanical properties. In order to achieve the required results in removing sulfur from the metal, it is necessary to analyze the main sources of sulfur input to the melt,

as well as technological factors affecting the desulfurization process for conversion in each process stage.

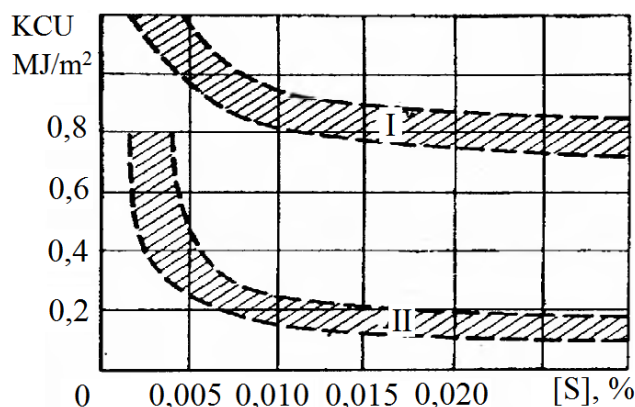


Figure 1. Dependence of impact hardness of aluminum deoxidized steel on content of sulfur determined for longitudinal (I) and transverse (II) samples of rolled products at room temperature.

3. Research results

The classical steel production scheme includes the following stages:

1. Obtaining of ore concentrate (ore production, sinter and pellets production).
2. Blast-furnace process (cast iron production).
3. External cast iron desulfurization.
4. Basic oxygen furnace process, steel production.
5. Steel processing in ladle furnace unit (LFU).
6. Metal processing at decreased pressure units.
7. Steel teeming in continuous-casting machines (CCMs).

At each stage, the sulfur content in metal will change, depending on the physical and chemical processes in the melting facility.

Depending on the chemical composition of cast iron, several special technological options are used to convert it into steel. JSC EVRAZ NTMK implemented vanadium conversion – processing of vanadium cast iron into steel and vanadium slag. The classic scheme is distinguished by the presence of a duplex process – a two-stage conversion. The first stage consists in extracting vanadium from cast iron and converting it as an oxide phase into slag. The result of this stage is the production of half-finished product (de-vanadium cast iron) and vanadium slag. After vanadium extraction, the molten metal with carbon content of 2.6–3.5 % goes to the converter for processing to obtain steel with a given chemical composition – this is the second stage. Between two stages of conversion, the half-finished product can be delivered to the desulfurization plant. Change of sulfur content in metal in stages of metallurgical conversion is given in Table 1.

Graphically the change of sulfur content and the degree of its change for conversion of production are presented in Figures 2 and 3.

The data presented in the figures show that the sulfur content after treatment at the desulfurization plant is 0.0068%, which is not sufficient to eliminate the effect of detrimental impurities on the service properties of the products. The minimum sulfur content in metal reaches the value of 0.0039% only with the complete metal treatment complex in the extra-furnace steel processing units – the ladle-furnace unit and the circulation vacuum vessel.

In order to study the sulfur partition (LS) between metal and slag in the LFU, let us compose a system of equations (1)–(3).

$$M \times [S]_0 + m \times (S)_0 = M \times [S]_f + m \times (S)_f \quad (1)$$

Where $(S)_0$ – initial sulfur content in slag (which is taken equal to zero); $[S]_0$ – initial sulfur content in metal; $[S]_f$ – final sulfur content in metal; $(S)_f$ – final sulfur content in slag; M – average heat weight (152.0 tons); m – mass of slag generated in the steel-pouring ladle of the LFU (1.98 tons).

Table 1. Sulfur partition in stages of manufacture of steel in case of different technology options.

Stages of manufacture of steel	Sulfur content in metal or raw materials, % wt.			
	Without treatment at the desulfurization plant		With treatment at the desulfurization plant	
	–	Treatment at the circulation degassing plant	–	Treatment at the circulation degassing plant
Obtaining of ore concentrate and fuel for blast furnace		Ore.....	0.006	
		Sinter and pellets (IORM).....	0.009	
		Coke.....	0.59	
		Pulverized coal fuel.....	0.34	
Blast-furnace process			0.0249	
Converter process 1.			0.0244	
Desulfurization of half-finished product	–	–	0.0068	0.0068
Converter process 2.	0.0196	0.0206	0.0083	0.0085
LFU (beginning of treatment)	0.0192	0.0196	0.0084	0.0086
LFU (end of treatment)	0.012	0.0126	0.0046	0.0057
Circulation vacuum vessel	–	0.008	0.0039	0.0057
CCM	0.012	0.008	0.0039	0.0057

$$L_s = \frac{(S)_f}{[S]_f} \quad (2)$$

$$\lambda = \frac{m}{M} \quad (3)$$

where λ – mass ratio of slag and metal.

Using equations 1–3, let us define the sulfur partition coefficient between metal and slag L_s :

$$L_s = \frac{\left(\frac{[S]_0}{[S]_f} - 1\right)}{\lambda} \quad (4)$$

Let us apply the formula 4 and the data of Table 1 for calculation of average values of the sulfur partition coefficient between metal and slag. Let us compare the calculated value $L_s=47.0$ with the data of sources [1] ($L_s = 50-100$) and [20] ($L_s \approx 50-250$). Despite the ‘satisfactory’ final sulfur content in metal (less than 0.005%), the steel manufacture technology including such stages as the treatment of the half-finished product at the desulfurization plant and the treatment of steel in the LFU and vacuum vessel, has reserves for the removal of sulfur. By adjusting the composition of the LFU slag, it is possible to increase their desulphurization capacity.

4. Conclusion

Thus, the current level of development of the industry requires the manufacture of steel with high purity in relation to detrimental impurities. Sulfur is one of the impurities that significantly reduces the service properties and the content of which in the finished product is strictly regulated. Deep desulfurization may be achieved through development of cross-cutting technology of metal production as a single process including agglomeration and blast-furnace process and steelmaking. Sulfur partition by metallurgical process stages via conversion from raw materials of the blast-furnace process to steel continuously cast blank is studied in this work. It is shown that removal of sulfur from the half-finished product at the desulfurization plant will not provide the required sulfur content (less than 0.005 %) in the steel ingot. It was determined that the activity plan comprising treatment of the half-finished product at the desulfurization plant, smelting in the converter, treatment of steel at the

ladle furnace unit and then in the vacuum vessel is required to obtain the final content of sulfur of less than 0.005%. According to the study of sulfur partition coefficient between metal and slag, despite the low final sulfur content in metal, this technology has reserves related to desulfurization achieved by correction of LFU.

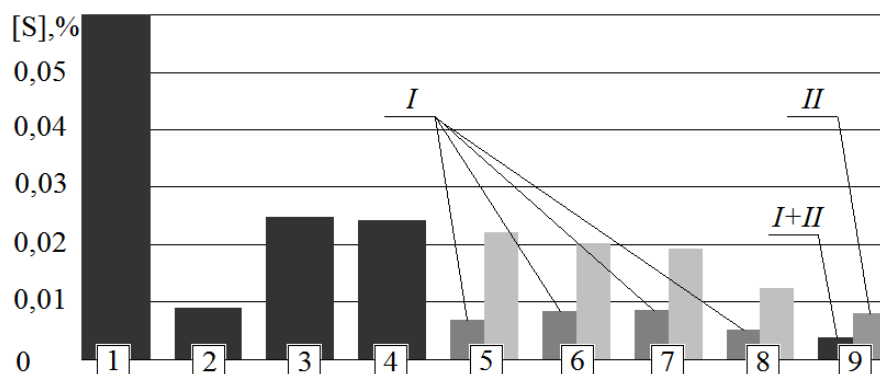


Figure 2. Diagram of sulfur partition in stages of manufacture of JSC EVRAZ NTMK, *I*– melts treated at the desulfurization plant, *II* – melts treated at the circulation vacuum vessel. Sulfur content in stages of manufacture: 1–in ore; 2 – in sinter; 3 – in cast iron; 4 – in half-finished product; 5 – desulfurization plant; 6 – at point of discharge from converter; 7 –deoxidation-alloying; 8 – treatment in LFU; 9 – treatment at RH.

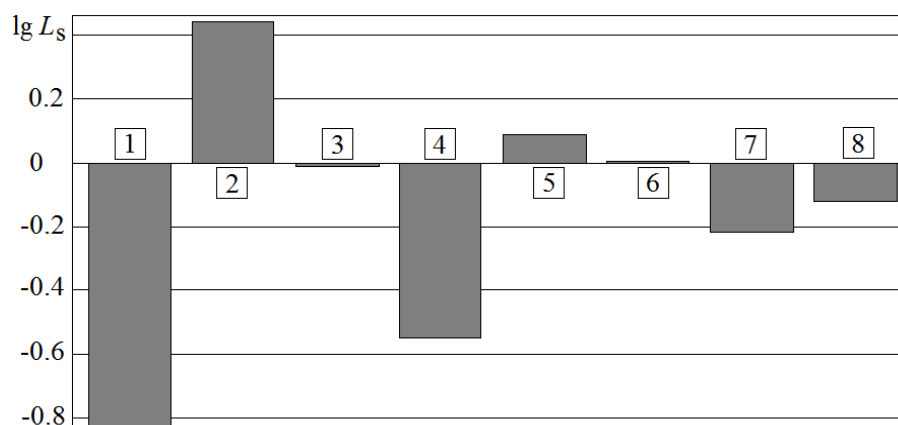


Figure 3. Changes in the sulfur content partition coefficient in stages of manufacture of JSC EVRAZ NTMK: 1 –Sintering production; 2 –Cast iron production; 3 –Vanadic conversion; 4 –Desulfurization of half-finished product; 5 –Steel conversion; 6 –Deoxidizing agents; 7 –Treatment at LFU; 8 –Treatment at RH.

References

- [1] Bigeev A M and Bigeev V A 2000 *Metallurgiya stali. Teoriya i tekhnologiya plavki stali* (Magnitogorsk : MG TU) p 544 (in Russian)
- [2] Ushakov A N, Bigeev V A, Stolyarov A M and Potapova M V 2019 Technology for production of pipeline ultra low sulfur steel *Chernye Metally* **12** pp 26–31
- [3] Ushakov A N, Bigeev V A, Stolyarov A M and Potapova M V 2018 Ladle Desulfurization of Converter Low-Sulfur Pipe Steel *Metallurgist* **62 (7-8)** pp 667–73
- [4] Ushakov A N, Avramenko V A, Bigeev V A, Stolyarov A M and Potapova M V 2018 Manufacture of Low-Sulfur Pipe Steel with Ladle Desulfurization of Cast Iron *Metallurgist* **61 (11-12)** pp 967–70
- [5] Gorkusha D V, Grigorovich K V, Karasev A V and Komolova O A 2019 Content modification

- of different types of nonmetallic inclusions during low-carbon if steel ladle treatment *Izvestiya Ferrous Metallurgy* **62 (5)** pp 345–52
- [6] Ghosh P, Ghosh C and Ray R K 2009 Precipitation in interstitial free high strength steels *ISIJ International* **49 (7)** pp 1080–6
- [7] Sheremet V A, Kekukh A V, Razdobreev V G, Kuvaev V N and Ivanov D A 2004 Influence of conditions of thermomechanical treatment on structures, mechanical and service properties of thermally strengthened reinforcing bars of A1000 class *Izvestiya Ferrous Metallurgy* **11** pp 40–3
- [8] Sheremet V A, Kekukh A V, Razdobreev V G, Kuvaev V N and Ivanov D A 2004 Influence of the thermomechanical-treatment conditions on the structure and properties of thermohardened class-A1000 reinforcement *Steel in Translation* **34 (11)** pp 59–62
- [9] Siyasiya C W and Stumpf W E 2008 The effects of hot rolling process and the nitrogen and sulfur content on the microstructural development of aluminium killed hot rolled low carbon strip steel *Journal of the South. African Inst. of Mining and Metallurgy* **108 (8)** pp 481–9
- [10] Li Y, Zhu F, Cui F and Fang K, 2007 Analysis of forming mechanism of lamination defect of steel plate *Dongbei Daxue Xuebao/Journal of Northeastern Univ.* **28 (7)** pp 1002–5
- [11] Yugov P I and Baeva L A 2004 Technological principles of the production of clean cold-resistant steels from pig iron with low contents of manganese and silicon *Metallurgist* **48 (7-8)** pp 307–10
- [12] Pike T J 2000 Production and metallurgy perspective of modern constructional steels *Proceedings of Annual Techn. Session, Structural Stability Research Council* 2000 pp 14–30
- [13] Tursunov N K, Semin A E and Sanokulov E A 2017 Study of dephosphoration and desulphurization processes in the smelting of 20GL steel in the induction crucible furnace with consequent ladle treatment using rare earth metals *Chernye Metally* **1** pp 33–40
- [14] Inaba S and Kimura Y 2004 Behavior of sulfur in the carbon-bearing iron oxide pellet during heating *ISIJ International* **44 (12)** pp 2112–4
- [15] Park J and Jung S 2016 Effects of various slag systems on metal/slag separation of CCA and slag composition on desulfurization and dephosphorization of iron nugget *Advances in Molten Slags, Fluxes, and Salts: Proceedings of the 10th International Conference on Molten Slags, Fluxes and Salts* pp 1025–30
- [16] Serov Y V and Mikhalevich A G 1982 Effectiveness of conversion pig improvement to meet steelmaking requirements *Metallurgist* **26 (2)** pp 37–43
- [17] Schrama F, Van den Berg B and Van Hattum G 2015 A comparison of the leading hot metal desulphurization methods *Proceedings of the 6th International Congress on the Science and Technology of Steelmaking, ICS 2015* pp 61–6
- [18] Schrama F, Van den Berg B and Van Hattum G 2015 Electric steelmaking: Comparing hot metal desulphurisation methods *Steel Times International* **39 (4)** pp 42–9
- [19] Bol'shakov V I, Shevchenko A F, Ye L D, Aleksandrov V A, Sen S T, Bashmakov A M and Trotsenko E A 2009 Rational ladle treatment for desulfurization of hot metal *Steel in Translation* **39 (4)** pp 326–33
- [20] Umezawa K and Kajioka H 1977 Slag metal reactions and refining abilities of the ladle furnace *Tetsu-To-Hagane/Journal of the Iron and Steel Institute of Japan* **63 (13)** pp 2034–42